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Surface reactions on beryllium after carbon vapour deposition and thermal treatment

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Abstract

Surface reactions and carbon layer formation on clean metallic beryllium are investigated in situ by X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectroscopy (RBS). The carbon is supplied by an electron beam evaporation device. The deposited films are successively heated to temperatures between 373 and 873 K in steps of 100 K and analysed after each step. After deposition at room temperature an amount of Be_2C up to 6×10^{15} cm^{-2} is present at the beryllium/carbon interface with elementary carbon on top. A first additional carbide formation takes place after heating to 473 K. For deposited amounts below 5×10^{16} cm^{-2} almost all carbon has reacted to carbide after the 673 K step. The carbidisation is complete at 773 K. Applying annealing times between 10 and 30 min characteristic Be_2C amounts build up for each temperature. Carbon diffusion into the bulk beryllium does not take place for temperatures below 773 K. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Beryllium; Carbon; Beryllium carbide; Material mixing

1. Introduction

A consequence of a multi-elemental first wall in fusion devices is the formation of mixed layers and compounds at the plasma facing components due to erosion and (re-)deposition processes. Beryllium has been used in JET and led to a significant improvement of the plasma performance and a substantial change of the first wall hydrogen inventory [1–4]. It is considered as a candidate first wall material for ITER along with tungsten and carbon [5]. Mixed beryllium/carbon materials exhibit altered properties regarding erosion and hydrogen retention with respect to the pure materials. Therefore, it is important to understand the surface reactions and the compound formation of carbon with beryllium at both room temperature and elevated temperatures. To minimise the influence of impurities (e.g., oxygen) sample preparation and in situ analysis has to be performed under ultra-high vacuum conditions. As we recently reported [6] vapour deposited carbon forms Be_2C at the beryllium/carbon interface at room temperature similarly to molybdenum [7] and tungsten [8]. We observed the first additional Be_2C formation at a lower temperature (473 K) than reported earlier (673–773 K [9–12]). In this paper we study the reaction of carbon layers with metallic beryllium after deposition and thermal treatment. We quantify the absolute carbide amounts at the different temperatures by combining the results of in situ X-ray photoelectron spectroscopy (XPS) and in situ Rutherford backscattering spectroscopy (RBS).

2. Experiment

A beryllium single crystal (0 0 0 1) was cleaned using 1 keV Ar^+ bombardment. The only detectable impurities after the cleaning process were oxygen (XPS: $<10^{14}$ cm^{-2}) and argon (RBS: $<10^{15}$ cm^{-2}). Carbon amounts between 0.18 and 10.42×10^{16} cm^{-2} (0.20 and 11.55 nm, assuming a density of 1.8 g cm^{-3}) were deposited on the substrate at room temperature using an electron beam evaporation device (Omicron EFM 3) and graphite (Goodfellow, 99.999%) as evaporant. Each film was heated in steps of 100 K from 373 to 873 K and

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kept at each temperature for 10 min. To investigate the influence of the heating duration, the sample remained at each temperature for 30 min in one series of measurements. After each step the sample was allowed to cool down for XPS (Mg K_α, 1253.6 eV) and RBS ($^4He^+$, 1 MeV, normal incidence, 165° scattering angle) analysis. The oxygen contamination of all films remained below 10^{15} cm^{-2} after the temperature treatment. For XPS an electrostatic hemispherical analyser (Physical Electronics, Ø 279.4 mm) was used. It is equipped with an entrance lens system and operated at a constant pass energy of 23.5 eV. The photoelectrons were detected at 90° relative to the sample surface and the Au $4f_{7/2}$ core level line (84.0 eV) of a clean gold sample was used for energy calibration. XPS C 1s spectra were fitted, using the MultiPak V 5.0 A code (Physical Electronics). For this fitting procedure (least-squares fit) each of the contributions has been approximated by a symmetric Gaussian/Lorentzian function centered at its characteristic binding energy. A Shirley-type background subtraction was applied to the spectra prior to the actual fitting procedure.

The base pressure in the new UHV chamber ARTOSS [13] and the pressure during RBS and XPS analysis was below 10^{-8} Pa. The pressure during carbon evaporation did not exceed 5×10^{-8} Pa. During the heating process the pressure stayed below 1.5×10^{-7} Pa for all temperatures.

3. Results and discussion

3.1. Carbon layer composition

As previously reported, C 1s XPS spectra measured after carbon vapour deposition on clean metallic beryllium showed three different components of the C 1s signal [6]: graphitic and disordered carbon (binding energies 284.2 and 285.2 eV, respectively [8]) and Be_2C (binding energy 282.1–282.6 eV).

The carbon signal composition as a function of the deposited carbon amount is shown in Fig. 1. For small coverages the majority of the carbon is bound in carbide. However, this Be_2C contribution decreases with an increasing deposited amount while the percentages of graphitic and disordered carbon increase to values of about 60% and 30%, respectively. This behaviour is explained by a limited carbide formation at the beryllium/carbon interface and the deposition of elementary carbon on top of the carbide. Assuming this model the measured carbide percentage decreases due to the limited information depth of the XPS technique. This limitation is due to the Lambert–Beer law which gives an exponentially decreasing probability for the emitted photoelectrons to escape from a certain sample depth according to their inelastic mean free path. The exponential-like behaviour of the Be_2 C percentage thus is a further confirmation of our model. The absolute carbide amounts after deposition at 300 K as a function of the total deposited carbon amount are shown in Fig. 4 by the 300 K curve. If the deposited carbon amount is large enough, then the carbide amount reaches a coverage-independent maximum of 6×10^{15} cm^{-2}. This amount is larger than a monolayer (about 10^{15} cm^{-2}) which may at least in part be due to an increased net surface caused by a considerable surface roughness. Also a deviation from the layer model that is applied to derive Fig. 4 (see Section 3.2) may lead to an error in the calculated amount. Because elementary carbon is present in the sample before the maximum amount of carbide is observed, the film is unlikely to grow layer by layer. That an island growth mode has to be preferred is also confirmed by the fact that during sublimation carbon clusters are formed which are unlikely to split and be mobile on the beryllium surface [14,15].

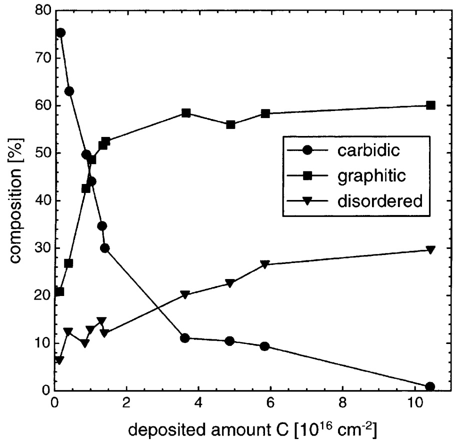

Fig. 1. Composition of the C 1s XPS signal as a function of the total deposited carbon amount after deposition at room temperature. Three different contributions can be distinguished: beryllium carbide (Be_2C), graphitic and disordered carbon.

Fig. 2 shows the results of XPS C 1s spectra fitting for a deposited carbon amount of 4.86×10^{16} cm^{-2} at each temperature step. The first additional carbide formation takes place after heating to 473 K. The XPS spectra show that a homogeneous carbide layer is present on top of the beryllium after the carbidisation is complete [6]. Thus a pure carbide layer on top of the beryllium substrate, growing in thickness with increasing temperature, can be assumed. Therefore, the first small additional carbide formation at 473 K may be due to two processes. The thickness of the carbide layer may simply grow. However, the deposited film is unlikely to grow layer by layer and thus the as-deposited interface is unlikely to consist of homogeneous carbide. Therefore, the formation of a homogeneous carbide layer at the interface would also explain a growing intensity of carbide.

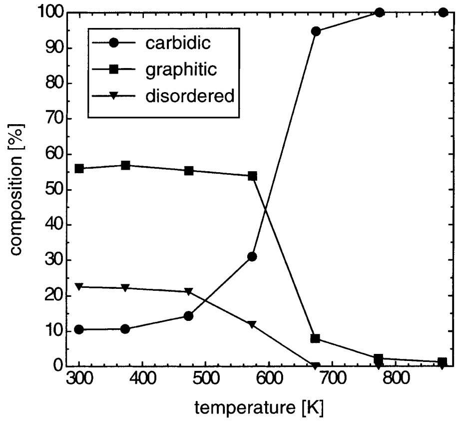

Fig. 2. Composition of the C 1s XPS signal after heating to the different temperatures for a deposited carbon amount of 4.86 × 10^{16} cm^{-2}. The three contributions are the same as in Fig. 1.

A more significant additional carbide formation takes place during heating to 573 K. These temperatures are lower than those reported in the literature, where a similar carbidisation of carbon on beryllium (diffusion of beryllium into carbon, respectively) is reported not to take place below temperatures varying from 673 to 773 K [9–12]. Because in the reported experiments either a different carbon modification was deposited (fullerenes [9]) or the samples were known to have a high oxygen contamination (at least 20% [10–12]), the lower temperature observed here can be explained by the very low contamination level of the samples. Moreover, all the carbon films studied in the cited publications have been too thick to allow a detailed investigation of the interface with the applied analysis techniques. This may also explain why the carbide formation during deposition at room temperature and the quantitatively small reaction after 473 K have not been observed before.

Above 473 K, the carbide percentage increases with increasing temperature. In the case of the smaller deposited carbon amounts (below approximately 2 × 10^{16} cm^{-2}) the carbidisation of the film is completed after heating to 673 K. For the bigger amounts (e.g., Fig. 2) the carbidisation is nearly complete at 673 K and at 773 K the entire deposited carbon has reacted.

Fig. 2 also shows that the percentage of graphitic carbon remains constant up to 573 K for a deposited carbon amount of 4.86 × 10^{16} cm^{-2}. However, the lowest deposited amount partly consists of graphitic carbon and has completely reacted to carbide at 573 K. This shows that there is no significant difference in the activation energies of disordered and graphitic carbon for carbide formation or carbon diffusion, respectively. Therefore, the observed temperature-dependent carbide formation is not due to different properties of these two carbon modifications.

3.2. *Be_2C quantification*

XPS results show an increase of the beryllium amount during the temperature treatment. This is due to the limited escape depth of the photoelectrons (and thus limited range of the analysis method) and to the beryllium diffusion into this analysis region during carbide formation [6]. The RBS measurements (Fig. 3) clearly show that the total carbon amount present on the sample remains constant. Each connected series of data points in Fig. 3 represents a different initial amount of deposited carbon and shows that this remains constant during the temperature treatment. Although a slight decrease of the carbon amount above 700 K is indicated by three of the series, there is no clear common trend. Besides these quantitative RBS results, the shapes of the carbon signals in the RBS spectra do not indicate a diffusion into the beryllium bulk either (symmetric shape remains, no low energy tail which would appear due to diffusion). This proves that the entire deposited carbon forms a Be_2C layer on top of the beryllium substrate. The stoichiometric composition of this layer has been reported in a previous publication [6].

Using XPS and assuming a layer structure (elementary carbon on top of Be_2C on top of beryllium), it is possible to determine the remaining amount of elementary carbon after each temperature step, if its thickness is in the order of the inelastic mean free path length of the emitted photoelectrons [6]. Subtraction from the respective total carbon amounts present (measured by RBS, see Fig. 3) gives the total amount of carbon bound

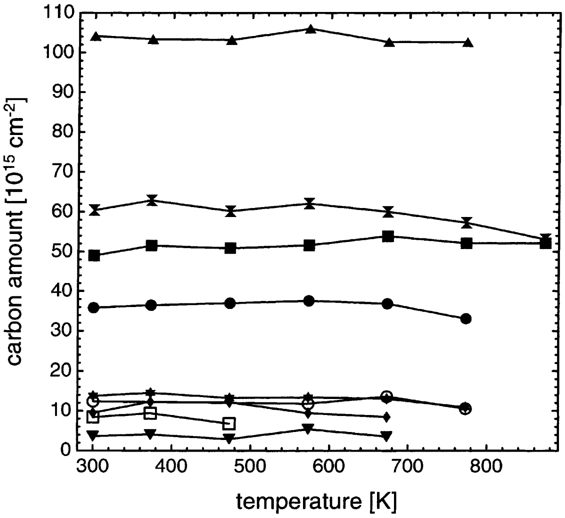

Fig. 3. Carbon amount, measured by RBS, present on the sample after deposition at 300 K and heating to the indicated temperatures. Each series of connected points (identical symbols) shows the development with temperature for a different deposited carbon amount.

in Be_2C after each temperature step. The results of this calculation are shown in Fig. 4. It shows that characteristic carbide amounts are formed for the following annealing temperatures: 300 K (after deposition), 373 K (no difference to 300 K) and 473 K. Although the 573 K curve does not reach saturation within the investigated region of deposited carbon amounts, it clearly shows a tendency to do so. For 673 K, the deviation from a complete reaction of the carbon is only very small but present for the higher deposited amounts.

Increasing the annealing time for each temperature to 30 min (instead of 10 min) does not change the limited carbide amounts observed for the different temperatures. This legitimates the assumption that either the reaction stops after the respective carbide amount has been formed or its time dependence is of a kind that does not lead to a significant change of the formed carbide amount within the annealing time difference applied here. In the literature a time-dependent diffusion of beryllium into the carbon film on a comparable time scale has been observed [10] and a nucleation process has been proposed to explain the rather rapid carbidisation of the films starting at temperatures above 673 K [12]. Because of the difference between the reported and observed temperatures the results are difficult to compare and it is difficult to assess at which temperature the first additional carbide formation takes place. Additionally, the deposited carbon amounts in these reported cases are much higher and the samples have a high oxygen contamination level, which may well be due to a BeO interface. If this is true, then the BeO interface may act as a diffusion barrier and thus influence the carbidisation process. Therefore, the understanding of the temperature and time dependence of the carbidisation process of thick carbon layers with a low contamination level on a clean beryllium substrate will be subject to further investigations.

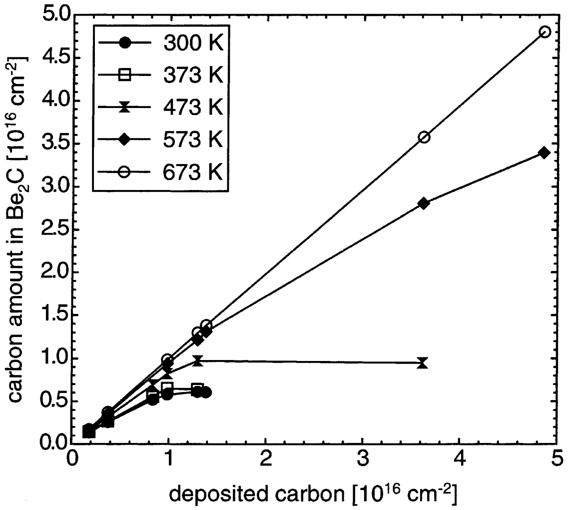

Fig. 4. Total amount of carbon bound in Be_2C at each temperature step as a function on the initially deposited carbon amount at room temperature. The data points measured at equal temperatures (but different samples) are connected to guide the eye.

4. Conclusions

It has been shown that during vapour deposition of carbon on clean metallic beryllium carbide is formed at the beryllium/carbon interface. The carbide amount is somewhat more than a monolayer. When exposing the deposited films to elevated temperatures the first additional carbide formation takes place during heating to 473 K, well below the temperatures so far known in the literature. For annealing times from 10 to 30 min the formation of limited carbide amounts, characteristic for each annealing temperature, is observed. The diffusion/reaction mechanism giving rise to this behaviour is not yet clear and needs further investigation. For deposited carbon amounts up to 5×10^{16} cm^{-2}, the carbidisation is complete after heating to 773 K and the entire deposited carbon amount is used to form a stoichiometric Be_2C layer on top of the beryllium substrate. No carbon is lost by diffusion into the bulk beryllium.

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