Release of Hydrogen Isotopes From Carbon Based Fusion Reactor Materials

Elizaveta Vainonen-Ahlgren

Accelerator Laboratory
Department of Physics
Faculty of Science
University of Helsinki
Helsinki, Finland

ACADEMIC DISSERTATION

To be presented, with the permission of the Faculty of Science of the University of Helsinki, for public criticism in the Large Auditorium of the Laurikainen Building, on June 17th, at 10 o'clock a.m.

HELSINKI 2000

Keywords (INSPEC): diffusion, migration, annealing behavior, diamondlike carbon, hydrogen, deuterium, silicon

ABSTRACT

The purpose of this study is to understand the annealing behavior of hydrogen isotopes in carbon based materials. Also, the density of the material and structural changes after thermal treatment and ion irradiation are examined.

The study of hydrogen diffusion in diamondlike carbon films revealed an activation energy of 2.0 eV, while the deuterium diffusion, due to better measuring sensitivity, is found to be concentration dependent with the effective diffusion coefficient becoming smaller with decreasing deuterium concentration. To explain the experimentally observed profiles, a model according to which atomic deuterium diffuses and deuterium in clusters is immobile is developed. The concentration of immobile D was assumed to be an analytical function of the total D concentration. To describe the annealing behavior of D incorporated in diamondlike carbon films during the deposition process, a model taking into account diffusion of free D and thermal detrapping and trapping of D was developed. The difference in the analysis explains the disagreement of activation energy (1.5 ± 0.2 eV) with the value of 2.9 ± 0.1 eV obtained for D implanted samples earlier. The same model was
applied to describe the experimental profiles in Si doped diamondlike carbon films.

Si affects the retention of D in diamondlike carbon films. The amount of D depends on Si content in the co-deposited but not implanted samples. Besides, Si incorporation into carbon coating decreases to some extent the graphitization of the films and leads to formation of a structure which is stable under thermal treatment and ion irradiation.

Hydrogen migration in the hydrogen and methane co-deposited films was also studied. In samples produced in methane atmosphere and annealed at different temperatures, the hydrogen concentration level decreases in the bulk, with more pronounced release at the surface region. In the case of coatings deposited by a methane ion beam, the H level also decreases with increasing temperature, and a concentration peak is produced at the surface region at 1100 °C.
Contents

ABSTRACT 1

1 INTRODUCTION 5

2 PURPOSE AND STRUCTURE OF THIS STUDY 9

3 FIRST WALL EFFECTS ON PARTICLE RECYCLING IN TOKAMAKS 12
  3.1 Basic particle-material interactions 12
    3.1.1 Reflection 12
    3.1.2 Implantation 13
    3.1.3 Sputtering 14
    3.1.4 Atomic defect production and trapping 15
    3.1.5 Re-emission 16

4 CHEMICAL EROSION 17
  4.1 Chemical erosion of carbon and carbon-based compounds observed in fusion reactors 17
  4.2 Chemical erosion due to hydrogen 19
  4.3 Chemical erosion due to oxygen 20

5 EXPERIMENTAL 21
  5.1 Sample preparation 21
  5.2 Ion beam techniques in the sample characterization 21
    5.2.1 Rutherford backscattering spectrometry 21
    5.2.2 Time-of-flight elastic recoil analysis 22
    5.2.3 Nuclear resonance broadening 23
1 INTRODUCTION

Energy production has always been a subject of great interest. All the energy sources used nowadays have some drawbacks. Oil, coal and gas increase the CO$_2$ amount in the atmosphere, which is now widely believed to lead to the climate changes [1–3]. Using wind, sun and water as energy sources is limited by the geographical areas where they can be applied. Nuclear fission power plants produce long-lived radioactive waste hazards. Controlled fusion is a solution for the “energy crisis” because of the availability and easy accessibility of an inexhaustible source of fuel for use in fusion reactors. Although it only exists as 1 part in about every 6500 hydrogen atoms, there is enough deuterium in ocean waters to satisfy the requirements in energy for millions of years.

There are other features of fusion reactors which make them especially attractive. The conditions required for energy production in a fusion reactor depend on the balance between certain parameters. If this balance is destroyed, the reactor will shut down automatically. Because of this, fusion reactor is safe against nuclear explosions, and has a lack of radioactive waste products compared to those in fission reactors. Tritium, needed in fusion reactors, does not exist in nature, so it should be produced. This can be done through nuclear reactions involving neutrons and lithium. Tritium, as a result of these reactions, will be fed into the reactor chamber. Contrary to fission reactors, there can not be any weapon material production in the fusion reactor. All the heat in the fusion reactor can be used to produce steam [4].

The structural materials of a fusion reactor must survive under high heat and radiation treatment. Fusion plasma contains high energy particles, and fusion reactions produce neutrons which modify the mechanical and physical properties of the structural materials. The most critical structural components of the International Thermonuclear Experimental Reactor (ITER) (see Fig. 1) are the first wall and blanket modules, and the divertor cassettes (Fig. 2).
Plasma-surface interactions lead to release of first wall atoms from the surface into the plasma. The plasma energy losses by radiation are lower for low-Z atoms than for high-Z materials like iron and nickel. Therefore in modern tokamaks, low atomic number Z materials, like carbon and beryllium, are used for plasma facing limiters and divertor plates. Carbon is the most widely used material because it has a better heat load resistance compared to metals. In some tokamaks carbonization was used to cover the initially metallic wall surfaces [6, 7]. Carbonization is a process where carbon is deposited onto the vessel walls by an RF assisted glow discharge in helium or hydrogen gas and methane. For the same purpose boronization was also used [8]. However, the carbon surface, as all low Z materials, suffers from a large physical sputtering yield and chemical erosion processes by hydrogen and oxygen. This can enhance the plasma contamination with carbon particles. In attempt to reduce the chemical interactions experiments with boronized carbon were performed in some tokamaks [8–11]. There is an investigation on Si doped carbon fiber material NS31 that shows decrease in the chemical sputtering by a factor of 2 to 3 compared to pure carbon [12]. In addition to this, Si doping will decrease the baking temperature needed to remove impurities from surfaces. Si is also known to
Figure 2: INTOR concept for blanket/shield structure with plasma-wall interaction controlled by a) a pumped limiter; b) a single-null poloidal divertor [5].
be a good oxygen getter and an impurity which increases thermal conductivity.

In the presence of plasma, redeposition of sputtered carbon particles, formation of diamondlike carbon films and carbon based composite films will take place. The uptake and release of deuterium and tritium from those films will significantly affect the recycling of D and T fuel as well as tritium retention in the fusion device. Therefore, an understanding of the processes which involve trapping and retention of hydrogen isotopes in those films is important. There is increasing interest in the application of silicon-containing materials for plasma facing components: siliconized layers, silicon carbides [13] or graphites doped with Si. Experiments on deuterium interaction with silicon-graphite materials [14] showed that less deuterium is accumulated on the C-Si substrate than on graphite. Due to the porosity of the mixture, some amount of D migrates from the surface layer into the bulk. Annealing in vacuum leads to the release of more than 99% of deposited deuterium.


2 PURPOSE AND STRUCTURE OF THIS STUDY

The aim of this thesis is to investigate retention and release of hydrogen isotopes in carbon films deposited in vacuum and in the presence of different substances (H, D, CH₄ and Si).

The organization of the thesis is as follows: in the present chapter a brief summary of the contents of the original publications is given. The publications will be referred to by Roman numbers and they are included at the end of this work.

In chapter 3 first wall effects on particle recycling in tokamaks are discussed and chapter 4 presents some remarks regarding chemical erosion of plasma facing materials. Experimental methods applied in the thesis and the sample preparation technique are described in chapter 5. The major results of the investigations are discussed in chapter 6 and the concluding remarks are given in chapter 7.

The experimental part of this thesis has been conducted at the Accelerator Laboratory of the University of Helsinki and at the Technical Research Centre of Finland. The author has done most of the experiments at the Accelerator Laboratory of the University of Helsinki, data analysis and has been responsible for the writing of the manuscripts of most of the articles.

Summaries of the original papers

Paper I: Hydrogen migration in diamond-like carbon films
E. Vainonen, J. Likonen, T. Ahlgren, P. Haussalo, J. Keinonen, and C.H. Wu

The migration of hydrogen in H⁺ and He⁺ ion-implanted and hydrogen co-deposited diamondlike carbon (DLC) films is studied with nuclear resonance broadening (NRB) and secondary ion mass spectrometry (SIMS) techniques. It is found that the annealing behavior of the implanted H has a diffusion like character with an activation energy of about 2.0 eV, and that co-implantation with He does not significantly affect the hydrogen diffusion.

Paper II: Concentration-dependent deuterium diffusion in diamondlike carbon films
T. Ahlgren, E. Vainonen, J. Likonen, and J. Keinonen
The diffusion of deuterium in DLC after thermal annealing was found to be concentration-dependent. The deuterium profiles, measured with SIMS, revealed that the effective diffusion coefficient decreases with decreasing deuterium concentration. This can be explained with the pairing model where deuterium pairs are considered immobile and atomic deuterium diffuses with an activation energy of about 2.9 eV.

**Paper III: Hydrogen in diamondlike carbon films**

E. Vainonen-Ahlgren, P. Tikkanen, J. Likonen, E. Rauhala, and J. Keinonen


Hydrogen behavior in the samples deposited in a methane atmosphere and by methane ion beam was studied. Annealing experiments show that release takes place by different mechanisms, which might be caused by the differences in the initial hydrogen concentrations.

**Paper IV: Stability of Si-C films prepared by a pulsed arc discharge method: Thermal treatment and heavy-ion irradiation**

L. Khriachtchev, E. Vainonen-Ahlgren, T. Sajavaara, T. Ahlgren, and J. Keinonen


Si-C films (Si content from 0 to 33 at.%) prepared in deuterium atmosphere at room temperature and at 400 °C were studied. The structural modification introduced by annealing up to 1100 °C, irradiation with 53-MeV \(^{127}\text{I}^{10+}\) ions, and deposition onto heated substrates are characterized by Raman spectroscopy. The results show Si-induced stabilization of the three-dimensional Si-C network.

**Paper V: Deuterium retention in Si doped carbon films**


Retention of deuterium was investigated in Si doped carbon films deposited in D atmosphere and implanted with D ions. The results show that Si content influences retention process in the samples deposited in D atmosphere but not in the implanted samples. This can be explained by formation of bonds between D and different target atoms. The release temperature for D in films not containing Si was found to be 984 °C.
PAPER VI: Deuterium diffusion in silicon doped diamondlike carbon films


Diffusion of deuterium in diamondlike carbon films with different Si content deposited in deuterium atmosphere was studied. A model was proposed to describe the experimental depth profiles. Diffusion, detrapping and trapping of D were taken into account in this model. Diffusion coefficient obtained for free D resulted in activation energies of 1.5 ± 0.2, 0.7 ± 0.2, 0.6 ± 0.2 and 1.2 ± 0.2 eV for samples containing 0, 6, 15 and 33 at.% of Si, respectively.
3 FIRST WALL EFFECTS ON PARTICLE RECYCLING IN TOKAMAKS

In the context of fusion reactors, recycling means all processes of particle and energy exchange between the plasma and the first walls of a fusion machine, i.e. limiters, walls, and divertor target plates. Particles which are lost from the plasma to the first wall, return back by reflection and re-emission from the material surface. The fraction of returned particles is between 90 and 100 %.

3.1 Basic particle-material interactions

One of the basic interaction processes between ions and material surfaces is elastic reflection at the surface. If the particle is not reflected, implantation into the bulk material takes place. Then the kinetic energy is lost in further collisions with the atoms of the host material. This can lead to creation of atomic defects in the lattice of the material and traps for the incident particle. Instead of being trapped, due to diffusion the particle can also either penetrate deeper into the bulk material or be transfered back to the material surface and re-emitted back into the plasma. Figure 3 gives a schematic overview of these processes.

3.1.1 Reflection

The process where a particle is re-emitted from surfaces back into the plasma without being involved in a retention process, can be named reflection. The process is based on scattering of the incident particle from the target atoms. In this case energy losses and momentum transfer take place. If the particle is scattered back to the surface and has an energy larger than the surface binding energy, it may escape from material.
Figure 3: Overview of some particle-surface interactions in plasma machines relevant to particle recycling: (1) elastic reflection; (2) implantation; (3) trapping/detrapping; (4) diffusion; (5) re-emission.

3.1.2 Implantation

If particles impacting onto a surface are not reflected, they will penetrate into the bulk of the material. Because the energy of the plasma particles bombarding the surface is well above thermal energies, the particle concentration in the material can be larger than the solid solubility limit under conditions of thermal equilibrium.

The slowing down of ions in a material is a stochastic process. When an ion penetrates into the material, it is involved into collisions with nuclei and electrons. Interactions between the incident ion and the material are divided into two mechanisms of energy exchange, namely electronic and nuclear collisions. In electronic collisions moving ion excites or ejects atomic electrons and in nuclear collisions energy is transferred to atoms as a whole.

In the general case, energy loss is a sum of nuclear and electronic energy losses. Nuclear energy loss becomes important at low ion energies while electronic energy loss dominates at higher ones. At
low energies (ion velocity \( v \) less than \( 0.1Z_1^{2/3}v_0 \), where \( v_0 \) is the Bohr velocity and \( Z_1 \) is the atomic number of the projectile) the slowing down ion is almost neutral and its energy loss is proportional to the ion velocity [15–19]. At high energies (\( v \gg Z_1^{2/3}v_0 \)) the ion is fully stripped of its electrons, the energy loss is inversely proportional to the square of the velocity [20, 21]. In the intermediate velocity region the ion is only partly stripped and theoretical treatment of the energy loss is the most difficult.

### 3.1.3 Sputtering

Release of atoms from the surface, which takes place when a hot plasma or a beam of energetic particles interacts with a solid, is called sputtering. The erosion at the surface by sputtering and implantation of particles can lead to changes in the composition and structure of the material. Thus, the lifetime of the walls of fusion reactor is determined by the sputtering.

At very high current densities and/or insufficient cooling of the target, the solid can be macroscopically heated and surface atoms can evaporate. Besides, implanted gas atoms can accumulate in the surface layers to form bubbles. This leads to blisters or flake formation and breaking of the surface layer. These two processes are not included in sputtering, which takes place at low fluences and low current densities [22].

If the incident ion transfers less kinetic energy than the threshold, which is about 10 to 40 eV for normal incidence, no sputtering takes place. Above this threshold, the mean number of atoms removed from the surface per incident particle increases with the incident energy and reaches a maximum in the energy region from 5 to 50 keV. When the incident energy is higher than that, the number of sputtered atoms decreases. In this case ion penetrates deeper into the solid and the energy deposited in the surface is low. Heavy particles cause higher sputtering yields than the ones with low masses.

If the bombarding particles do not react chemically with the atoms of the solid, a surface layer will be damaged within the ion range and some ions will be trapped [23]. In the case of bombardment
with reactive ions, formation of a compound surface layer which has a different composition than the initial material occurs [23]. Sputtering effects will be similar to those in the compound formed.

If a volatile compound is formed on a surface (like CH₄ or H₂O with hydrogen ion bombardment), sputtering yields are increased at temperatures where the molecules desorb at the surface. The sputtering yield can be decreased, if a very stable solid compound is formed on the surface, for example a carbide or an oxide for carbon or oxygen bombardment, respectively.

### 3.1.4 Atomic defect production and trapping

Hydrogen implantation into carbon, at energies of around 100 eV leads to atomic trapping of hydrogen. At room temperature the maximum possible ratio of hydrogen to carbon is about 0.4 (29 at.%) [24].

Hydrogen trapping has been investigated by ion beam experiments. Results show that the concentration of trapped hydrogen increases over the whole range distribution. When the local saturation concentration is reached at some range, the concentration increases only at non-saturated places, until saturation is reached over the whole depth distribution. Then no further increase of the concentration of the trapped particles takes place.

During bombardment atomic defect production occurs. This process competes with annealing of lattice defects due to the mobility of interstitials and vacancies and their recombination [25]. However, if an implanted atom occupies vacancy, the defect can be stabilized and recombination with interstitials will stop. Because particle flux densities and fluences are high on the target plates of tokamaks, recombination rates may not be high enough to anneal all the damage. This can lead to production of damage which results in the amorphization of surface layer. Hydrogen and helium trapped in material can form high pressure bubbles, which when they grow can destroy the material by creating cracks to the surface which makes the release of particles from the material easy.
The effect of precipitates on H trapping in metals has also been studied [26–31]. The annealing of helium-implanted samples at elevated temperatures showed that the trapped solid soluble hydrogen was released, indicating the He damage recovery. The proposed mechanism is trapping at the interfaces between the precipitate and the metal by implantation or ion-irradiation induced vacancies: vacancies are trapped by the precipitate and form an open volume at the precipitate-metal interface. Hydrogen then fills this volume. Observation of the critical dose, above which the H concentration does not increase with the He dose but stays below the saturation level, proves the assumption that the H trapping takes place at the surface of the He precipitates [32, 33].

Except atomic trapping at the implanted region of the material, in graphite it was observed [34, 35] that hydrogen is also trapped by up to about one atomic percent within the bulk material, at depths far beyond the range of energetic particles. The precise mechanism of this process is unclear but it was suggested that due to the open crystal structure of graphite, diffusion of molecular hydrogen leads to the deeper penetration with following trapping at intrinsic defects.

### 3.1.5 Re-emission

If the particles impacting the material are not trapped in the implantation region, two processes are possible. The first one is their escape and re-emission. In the second case, the particle penetrates deeper into the bulk and is trapped there. In ion beam experiments with bombardment of carbon targets to very high fluences \(10^{19} \text{ cm}^{-2}\) and the measurement of the following thermal outgassing [35] it was observed that hydrogen release increased above the level expected due to the trapping in the implantation region.

Transport of hydrogen in carbon is not well understood. A study with different hydrogen isotopes in graphite [36] suggested that hydrogen transport at temperature below 1300 K occurs due to molecular diffusion. To describe the release of hydrogen from materials in a simple way, diffusion through the bulk material and recombination at the surface should be considered [37, 38].
4 CHEMICAL EROSION

During plasma-wall interactions in fusion devices, the chemical reactions of plasma particles, i.e., hydrogen isotopes or plasma impurities, with wall materials can lead to the formation of volatile molecules. This process is referred to as chemical sputtering or chemical erosion. Chemical sputtering involves the presence of at least one species of energetic particles (reactive or inert) while chemical erosion can also include reactions due to thermal atoms only. Chemical sputtering includes the implantation of reactive particles into wall materials, which can result in possible surface modification and changes of material properties, molecule formation, and molecule desorption.

When volatile molecules emitted from the walls enter the plasma, they become ionized and can be either directly redeposited on the wall or act as impurities in the plasma. Impurities in the plasma lead to a decrease in the number of ions available for fusion reaction and increase of radiation losses. The radiation loss level depends on the atomic number $Z$ of the impurities ($\sim Z^2$ to $Z^4$). Carbon has a relatively low atomic number, which makes it attractive for application in fusion device. However, the main disadvantage of carbon based materials is their easy erosion under plasma exposure and their ability to retain hydrogen. The strong carbon erosion results in contamination of the plasma with carbon particles and reduces the life-time of first wall components.

4.1 Chemical erosion of carbon and carbon-based compounds observed in fusion reactors

Interaction of the hydrogen fuel and oxygen impurities with carbon or carbon based material results in chemical erosion of the walls of the fusion device. The formation of water is also possible. The energy and fluxes of the impacting particles, surface temperature and near-surface properties of the plasma facing carbon material affect the contribution of different chemical reactions to the total carbon erosion.
The formation of hydrocarbons in tokamaks has been observed by the method of residual gas analysis [39] and by optical emission spectroscopy in front of limiters [40]. These effects play an important role in the production of impurities in the divertor region of tokamaks, where densities are high and ion temperatures are low. For the modeling of impurity behavior in the limiter region in JET [41] and JT-60U [42], in addition to physically sputtered carbon atoms, a hydrocarbon formation yield of $0.02 - 0.05 \text{CD}_{2}/D$ has to be assumed.

Oxygen plays a crucial role in the lifetime of a fusion device and a lot of effort has been made to reduce oxygen contamination in the form of CO and CO$_2$ [40]. If wall conditioning and gettering are not efficient, oxygen and carbon fluxes dominate all other impurity sources in the plasma [43, 44].

There have been attempts to reduce chemical erosion effects and the plasma contamination by introducing dopants into the carbon matrix. The improvement has been achieved due to the lowering of chemical erosion of carbides under impact of hydrogen ions [45]. However, the question of the central interest is the oxygen-gettering behavior of the dopants; i.e. their oxides are not volatile. This effect has been observed by titanium gettering [46], boronization [8, 47], beryllium evaporation [48], and siliconization [49]. By the use of the boron-containing carbon in TEXTOR (Tokamak EXperiment for Technology Oriented Research), the reduction of oxygen was obtained to be more than a factor of 3 compared to normal carbonized wall conditions [46, 50]. Carbon was reduced by a factor of 2, and the boron content was less than that of carbon [46]. Unfortunately, the main drawback of dopants is the decrease of the thermal conductivity of carbon material compared to undoped one. However, a silicon doped carbon fiber composite with an optimized thermal conductivity has been developed [51].

In the divertor region protective surface layers erode within a few seconds during a discharge. Therefore, methods are needed to replenish the surface concentration of dopants in plasma facing materials in order to provide oxygen gettering and/or reduced chemical erosion during operation.
One possibility is to use bulk-doped carbon materials, which provides a continuous supply of surface dopants [52], another method involves controlled reactive gas puffing into the divertor region.

### 4.2 Chemical erosion due to hydrogen

In the case of hydrogen ion impact, there are two branches of the chemical erosion of carbon: a high temperature branch with the maximum yield at \(\sim 750 \text{ K} \), and a low temperature branch below 500 K. In the latter case, the yield increases with decreasing ion impact energy. The low temperature branch of the hydrocarbon formation due to hydrogen impact in carbon materials is observed in ion beam experiments as well as in the high flux region of the scrape-off plasma in TEXTOR [53]. This reaction channel is not reduced by boron doping, and is especially important in low temperature plasma, for instance in the divertor region where hydrocarbon formation seems to be the main erosion process. The high temperature branch becomes broader with decreasing hydrogen impact energy, and the maximum yield increases with increasing hydrogen impact energy (up to 300 eV). Ion beam experiments at low energies (\(\leq 1 \text{ keV} \)) are typically done using fluxes below \(10^{16} \text{ cm}^{-2}\text{s}^{-1} \). While this value is similar to ion fluxes on first wall components in tokamaks, fluxes on limiters and divertors can be two to three orders of magnitude higher. Therefore, an important parameter for the projection of beam results to limiter/divertor conditions is the flux dependence of erosion.

Standard models describing the sputtering and erosion of materials by ion bombardment assume that the sample composition remains constant during the bombardment and the erosion yield per incoming ion is independent of the ion flux. Very recent experiments, however, show that during conditions of extremely high-flux hydrogen bombardment the erosion yield of carbon drops by at least an order of magnitude between fluxes of \(10^{18} \text{ – } 10^{20} \text{ ions/cm}^2\text{s} \) [54, 55].

Recent molecular dynamics simulations [56] show that the reason for the drop in the carbon erosion yield at high fluxes is the formation of a layer with high hydrogen content within the first 1 nm from
the surface. This leads to a shielding of carbon atoms by hydrogen and hence a decrease in the cross section of collisions with carbon atoms.

4.3 Chemical erosion due to oxygen

The impact of oxygen ions on carbon leads to the formation of CO and CO$_2$. The associated erosion yield is $\sim$0.7 eroded C/O, almost independent of the O$^+$ impact energy (0.25 – 5 keV) and carbon temperature [57]. The chemical erosion due to oxygen contamination is often the dominant erosion process in pure carbon tokamaks. The plasma performance in tokamaks can be highly improved by using carbon based materials doped with elements able to act as an oxygen getter. The reduction of the oxygen impurity level in tokamak discharges can be explained by the low reaction rate and the high oxygen retention of B-containing carbon which was observed during O$^+$ impact studies in ion beam experiments.
5 EXPERIMENTAL

5.1 Sample preparation

Carbon based or diamondlike carbon (DLC) films used in this study were made by the company DIARC-Technology Inc. using the arc discharge method. The substrate was cleaned by argon etching. Mostly single ionized carbon plasma is generated and accelerated by an arc discharge between a graphite cathode and an anode and directed to the substrate using magnetic filtering.

The deposition process takes place at a temperature of 60 °C in a vacuum (~ 0.5 mPa) or in an atmosphere of different gases (hydrogen, deuterium or methane). The samples can also be grown by using a methane ion beam. In this case the coatings were made directly from methane gas by establishing a gas flow through a broad-beam ion source developed by DIARC-Technology Inc. The average energy of a CH$_4$-molecule was approximately 250 eV and the deposition rate about 0.8 µm/h. Samples with different silicon content were also grown. These films were produced from a cathode made by mixing pure graphite and silicon powders which were further solidified by hot isostatic pressing technique.

5.2 Ion beam techniques in the sample characterization

The obtaining of the elemental composition of a sample is one of the main analysis problems in materials research. Ion beam techniques can successfully be used for this and other purposes as well.

5.2.1 Rutherford backscattering spectrometry

Since its development in the first half of the 20th century Rutherford backscattering spectrometry (RBS) has become the most commonly used ion beam technique in materials science. Ease of the analysis, non-destructiveness and the ability to simultaneously determine the depth distribution
of several atomic species below the surface are advantages of the method. Combined with ion channeling, RBS becomes a powerful tool to detect crystalline defects in single-crystal materials, such as semiconductors. RBS is especially suitable for the determination of depth distributions of heavy elements in lighter substrates, where other analysis methods fail.

RBS is based on the Coulomb interaction between the target atom and the incident ion. The mass resolution of RBS is determined by the kinematic factor, which is the ratio of the incident ion energy after and before an elastic scattering event. The kinematic factor depends on the masses of the incident ion and target atom and on the geometry of the experiment. Isotopic resolution can be achieved for light target atoms with proper choice of ion, beam energy and experimental geometry.

The depth scale of an RBS measurement is related to the energy of the detected backscattered ion and its energy loss in the analyzed material. Typically the depth scale ranges from a few nm’s up to several μm’s. The depth resolution is typically 5 - 15 nm at sample surface. The detection limit depends on the scattering cross section, which has a $Z^2$ dependency for the incident and target nuclei [58]. In combination with SIMS, RBS was used for density measurements in Papers I, III and IV. The Si concentration was obtained from the results of the RBS experiments in Papers IV - VI.

5.2.2 Time-of-flight elastic recoil analysis

Another technique which can be used for depth profiling of different elements is elastic recoil detection analysis (ERDA). The method is similar to RBS. The difference is in the mass ratio for incoming and recoil ions. In ERDA a heavy projectile is used to kick out light target atoms.

The main experimental problem is to separate the signals originating from the recoiling atoms of different elements from each other and from those of the scattering primary ions. In the conventional ERDA method stopping foils are used for the separation [59]. A foil (typically about 10 μm thick mylar) is situated in front of the energy detector, and its thickness and material are selected so that
scattered primary ions and in many cases also bulk atoms and other recoiled heavy atoms are absorbed in the foil. In some cases a foil can be used to separate overlapping signals of different elements, for example H and He [29], due to different stopping powers of these elements and therefore different shifts in the measured energy spectrum. However, the foil causes energy straggling to the recoil atoms, thus leading to a worse depth resolution.

One of the most promising ERDA configurations in many applications is the time-of-flight ERDA (TOF-ERDA) detection system [60–62]. In this set-up the time-of-flight of each particle is measured over a known flight path in coincidence with the conventional energy spectrum. The mass of each detected particle is calculated from the classical relation for kinetic energy. In the case of TOF-ERDA thick foils that cause energy straggling and therefore poor depth resolution are not needed.

ERDA and TOF-ERDA techniques were used to measure content and composition of the samples in Papers I, III, IV, V and VI.

5.2.3 Nuclear resonance broadening

Nuclear resonance broadening (NRB) was used to determine the depth profiles of hydrogen atoms in carbon films. NRB analysis is based on the resonance reaction of the incident ion and target nucleus. The width of the resonance should be small enough to enable good depth resolution. Narrow resonances are usually found in the excitation curves of light isotopes. For an example of resonance reactions and their strengths see Keinonen et al. [63].

In an NRB measurement the γ-ray yield from the chosen resonance reaction is measured as a function of the incident ion energy. The absolute concentration of an isotope is deduced by measuring the γ-ray yield from a reference sample with a known isotope concentration. The depth scale is determined by the stopping of the incident ion, similarly to RBS. The detection limit will depend on the resonance reaction cross section, and the depth resolution on the energy straggling of the incident ion and on the
energy width of the resonance. Typically concentrations of approximately 0.1 at.% can be measured, and the depth resolution is of the order of a few nm’s at the surface. Computer programs have been developed to convert measurements of gamma yield versus beam energy to depth profiles [64–68]. For the depth profiling of H atoms NRB technique was used in Papers I and III.

5.2.4 Particle induced X-ray emission

Particle induced X-ray emission (PIXE) analysis is based on the ejection of inner shell electrons from the target atoms as high-energy particles interact with them. When the vacancies are filled by outer shell electrons, the energies involved in the transitions fall in the X-ray region of the electromagnetic spectrum. The X-ray energies are characteristic for the elements and the X-ray intensities are proportional to the number of atoms present in the sample. Hence, the sample elements may be identified and their concentration deduced from a characteristic X-ray spectrum, as was done in Papers I and III. The detection limit of PIXE is affected by $\gamma$-ray background and bremsstrahlung due to the incident particles and secondary electrons.

5.2.5 Doppler shift attenuation

Conventionally Doppler shift attenuation (DSA) method is used for the determination of short nuclear lifetimes ($\sim 10^{-15} - 10^{-11}$ s). However, if the lifetime is known the method can be used for the determination of the sample density [69], as was done in Paper III.

The main principle of the DSA method is as follows. When nuclear reactions are generated with a particle beam bombardment, the recoiling excited nuclei travel in a fixed direction and stop gradually in the backing material. If the lifetime of the excited state is the same order of magnitude as the time of the slowing down, $\gamma$-rays will be emitted during the de-acceleration process. At the moment of emission the recoiling nuclei have different energies. Due to the Doppler effect, this results in different energies of $\gamma$-rays. The rate of the slowing down of recoiling nuclei is proportional to the
density of the backing material, which in turn means that the measured profile of the $\gamma$-ray peak depends on the density of the backing material.

When the DSA method is used for carbon, no $(p,\gamma)$ reaction with suitable nuclear lifetimes exists for the most abundant isotope $^{12}\text{C}$ (98.9%). However, the carbon isotope $^{13}\text{C}$ (1.1%) has a suitable resonance in the $^{13}\text{C}(p,\gamma)^{14}\text{N}$ reaction at $E_p = 1150$ keV strongly populating the 2313 and 6204 keV states which have suitable lifetimes [70]. In this case the $\gamma$-rays peaks are seen as a combination of two components when the DSA measurements are performed at an angle of 0° with respect to the beam direction: a low energy peak due to the fully stopped recoils and a high energy peak due to the recoils in full flight.

### 5.2.6 Secondary ion mass spectrometry

In Papers I - VI secondary ion mass spectrometry (SIMS) is applied for the depth profiling of the hydrogen and deuterium atoms. In typical SIMS measurements a primary ion beam is raster scanned over an area ranging from $100 \times 100 \text{ \mu m}^2$ to $500 \times 500 \text{ \mu m}^2$. Primary $\text{O}_2^+$, $\text{Cs}^+$, $\text{Ar}^+$, $\text{Kr}^+$ and $\text{Xe}^+$ ions with energies of 1 to 50 keV are used. Collisions between the primary ions and the target result in the release of atoms and molecules from the target into vacuum. A small fraction of the released atoms and molecules are ionized. These ions are extracted with an electric field and analyzed with a mass spectrometer. The depth scale of the SIMS spectrum is determined by measuring the depth of the induced eroded crater in the sample with a profilometer. The sputtering rate can then be calculated when the elapsed measurement time is known. The mass resolution of SIMS is good enough to distinguish isotopes of an element from each other and depending on the studied impurity, concentrations of $10^{13}$ to $10^{15}$ at./cm$^3$ can be detected [71].
5.3 Measurements of bonding structure

Because the amount of tetrahedrally oriented sp$^3$ bonds inside the carbon film has an influence on sample properties, the measurements of bonding structure (sp$^3$/sp$^2$-ratio) is necessary for the sample characterization. A possible technique for this kind of measurements could be electron spectroscopy for chemical analysis (ESCA). In such experiments the sample is irradiated with monochromatic X-rays, the energy of which is transferred to the bound electrons of the target atoms. Photoelectrons have enough kinetic energy to reach the sample surface. By the measurement of the energy of the escaped electrons it is possible to determine the electron binding energy inside the sample.

Raman spectroscopy can be used for qualitative and quantitative investigations of hard amorphous and diamondlike carbon films [72–75]. The samples are irradiated with a monochromatic laser light (in this thesis a 50 mW Ar laser at 514.5 nm was used [V]). The original photon quantum may be reduced or augmented. The observed difference in the wavelength is accounted as the Raman shift. By analysing Raman spectra it is possible to obtain an information about the bond configurations.
6 SUMMARY OF RESULTS

It was already earlier indicated that \textit{ex situ} surface analyses of first wall structures in tokamaks with carbon surfaces [76–78] showed the presence of thick (\(\mu\)m) layers of deposited carbon material saturated with hydrogen. As these layers were mostly located in regions with only little direct plasma contact and because the thickness exceeded by far the projected range (\(\sim 5\) nm) of energetic hydrogen in carbon, it was therefore concluded that simultaneous deposition (co-deposition) of carbon (previously eroded at limiters for instance) and hydrogen caused the formation of these layers. The possible contribution of co-deposition to the general hydrogen pumping in the Joint European Torus (JET) was presented for constant plasma conditions [79]. The results suggested that co-deposition may have a noticeable (though not dominant) contribution to the density decrease which takes place when the external gas supply is switched off. However, it is unlikely to be the only process by which hydrogen is pumped in carbon-dominated tokamaks, because otherwise there would be no outgassing. Co-deposition should provide a permanent removal of hydrogen by trapping. Surface analyses also showed that in regions with direct contact between plasma and material surfaces [77], the hydrogen content is typically more than an order of magnitude lower than in the regions with co-deposition and therefore the hydrogen content is determined by implantation only.

6.1 Diffusion of hydrogen isotopes

In Papers I and II annealing behavior of implanted hydrogen and deuterium in carbon films deposited in vacuum was studied. The one dimensional diffusion equation is suitable to describe this process and to get the time dependence for the concentration of diffusing atoms. This equation is also called the \textit{second law of Fick} [80], where the change of the concentration \(C\) [atoms/cm\(^3\)] in time \(t\) is the difference of the fluxes between the two atomic rows divided by their distance,

\[
\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}(D \frac{\partial C}{\partial x}),
\]  

(1)
Figure 4: Experimental deuterium depth profiles obtained after implantation and after annealing at different temperatures with numerical fits by the diffusion model (dashed line) [II], and by error function (dot-dashed line). The dotted line is the deposited energy calculated by SRIM-96 computer code [81]. The inset shows deuterium diffusion length vs square root of the annealing time. The solid line is the linear fit to the experimental data.

where $D \, [\text{cm}^2/\text{s}]$ is the diffusion coefficient. If $D$ is constant, i.e. $D$ does not depend on time, position or concentration, Eq. (1) becomes

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2}\right),$$

which is usually called the concentration independent diffusion equation, and can be solved analytically in some cases. Otherwise the diffusion is called concentration dependent.

In the case of hydrogen implanted carbon films diffusion was found to be concentration independent [I]. The diffusion activation energy $E_a$ and pre-exponentional factor $D_0$ are $E_a = 2.1 \pm 0.1 \, \text{eV}$, $D_0 = 1.3 \times 10^8 \, \text{nm}^2/\text{s}$, respectively.

Contrary to that, the diffusion of D in carbon films was found to be concentration dependent, as shown in Fig. 4, where the diffusion profiles after annealing at 900 and 1000°C are depicted. As seen in the figure the deuterium diffusion profile starts to deviate from the complementary error function at concentrations below 0.07 at.%, where the effective diffusion coefficient slightly decreases with concentration (see Fig. 1 in Paper II). This diffusion behavior was explained by assuming that some
deuterium atoms form immobile pairs and that the remaining atomic deuterium diffuses, with an activation energy of 2.9 ± 0.1 eV. For hydrogen diffusion in carbon films no concentration dependent diffusion was observed due to the high hydrogen background and the poor measuring sensitivity compared to that of deuterium. In general, for two isotopes, with masses $m_1$ and $m_2$ of a given element, the activation energies should be the same, and their pre-exponential factors should differ by a factor of $\sqrt{m_1/m_2}$ due to the isotope effect [80]. By employing the matrix method, which is described in Paper I, to fit D profiles and choosing the lowest concentration limit of 0.07 at.% one gets an activation energy of 2.0 ± 0.1 eV, matching the value obtained for H. The ratio of the pre-exponential factors for H and D in this case is 1.3, which comes from the isotope effect.

Mehandru, Anderson and Angus [82], studied theoretically hydrogen binding and diffusion in diamond. They observed that H at a bond-centered (BC) site is more stable than at the tetrahedral and hexagonal interstitial sites and that BC hydrogen diffuses along the high-density (110) planes with an activation barrier of about 1.9 eV. They also suggest that a second hydrogen atom forms an even more stable bond to the nearby antibonding (AB) site, forming a BC - AB hydrogen pair, which supports the use of the present pairing model.

6.2 Annealing of hydrogen and methane co-deposited films

In the hydrogen [I] and methane [III] co-deposited films, hydrogen migrates towards the interface between the film and substrate, and is also released from the surface region. The overall amount of hydrogen decreases as a function of annealing temperature as well.

In Paper I samples grown in hydrogen atmosphere at different deposition pressures were also studied. For the depth profiling of H atoms NRB technique was used. H concentrations in the samples deposited at different pressures were relatively constant throughout the film. It was found that the hydrogen content is proportional to the square root of the deposition pressure.
Annealing experiments showed a decrease of the hydrogen concentration with increasing temperature, via H release and migration to the interface (see Fig. 4 in Paper I). It was observed that the release temperature varied between 950 and 1070 °C depending on the H concentration.

Hydrogen annealing behavior in samples deposited in methane atmosphere and by using a methane ion beam was also investigated [III]. For depth profiling of H, the NRB technique in combination with SIMS experiments was used. In methane co-deposited films, migration of hydrogen with increasing temperature takes place (see Fig. 5). A remarkable H release from the surface region occurs upon annealing. There is also a noticeable change in the profile shape at the interface region corresponding to the peak in the H concentration.

In samples deposited by methane ion beam, hydrogen behaves differently with temperature increase compared to samples deposited in methane or hydrogen atmosphere. The overall amount of H decreases as a function of increasing annealing temperature. At 1100 °C there is, however, a peak at the surface region of the profile. For all annealing temperatures the hydrogen content in the bulk decreases evenly without producing any peak at the interface.
6.3 Si doped carbon films

Si co-deposited carbon films were investigated to understand Si influence on hydrogen isotope retention and release. In addition to samples produced at room temperature, coatings deposited at 400 °C were studied.

By the use of Raman spectroscopy it was found that the introduction of Si stabilizes the three-dimensional Si-C network. The Si incorporation decreases to some extent graphitization of the material in annealing. An extensive graphitization process is observed for the Si-free DLC films at 900 °C but the process is quite minor when the Si concentration is 33 at.%. In annealing at 1000 – 1100 °C, the Si-C three-dimensional structure collapses to pseudo-graphite. The incorporation of Si also decreases graphitization when the material is deposited onto a heated substrate (400 °C).

The Si-C network is also stable under exposure to energetic (53 MeV) iodine ions, which were used for TOF-ERDA analysis. For the Si concentration of 33 at.%, the result of ion irradiation is essentially independent of preliminary annealing. This observation introduces the recovery of thermally collapsed structure by the ion milling.

6.3.1 Deuterium retention

The dependence of the amount of retained deuterium on the Si concentration was investigated in the films deposited in deuterium atmosphere and implanted with D ions. As can be seen in Figs. 6 and 7, the process is different in these two sets of samples. The possible explanation of the difference is the formation of bonds between D and target elements. In the case of samples deposited in deuterium atmosphere, D saturates dangling bonds of Si atoms at the surface during the growth process, producing the ideal Si sp³ bonding configuration. That is the possible reason why the Si content affects the amount of retained D. Implantation of D in a ready target, on the contrary, means that all bonds are already formed. The most likely process due to which D stays in the sample is a
reaction with an sp\(^2\)-bonded carbon atom, which then enters into the sp\(^3\) state. In this case the Si content does not influence retention.

### 6.3.2 Deuterium diffusion in Si doped films

To describe the annealing behavior of D in Si-DLC, a diffusion model was proposed in Paper VI. This model takes into account diffusion of free D, thermal detrapping and trapping of D atoms. The Arrhenius plots obtained for diffusion coefficients of free D in Si-DLC and for implanted D atoms (Paper II) are presented in Fig. 8. Activation energies were 1.5 ± 0.2, 0.7 ± 0.2, 0.6 ± 0.2 and 1.2 ± 0.2 eV for samples containing 0, 6, 15 and 33 at.% of Si, respectively. The activation energy obtained for Si-free coatings is different from the one obtained for D implanted samples in Paper II \((E_a=2.9 \pm 0.1 \text{ eV})\). Further study is needed to explain this discrepancy. Contrary to the calculations employed for Si doped films, in the model used in Paper II the immobile or trapped D was assumed to be an analytical function of the total D concentration. This simplifies the calculations of diffusion of the implanted D.
Figure 7: Amount of retained D as a function of implantation dose in samples with different Si concentrations. The solid line presents an ideal case when all implanted deuterium is trapped. Dots show the implantation doses used.

Figure 8: Arrhenius plots for diffusion coefficients of free D in Si-DLC films and atomic D in Si-free coatings.
7 CONCLUSIONS

The conditions necessary for operating a fusion device are high enough temperature and density of the plasma. Achieving these properties is strongly dependent on plasma contamination, i.e. how ions and neutral atoms absorbed in the walls of the device are emitted back to the plasma, and interact with other atoms of the wall material. Hence, understanding and controlling the retention and release of hydrogen isotopes are the key points of fusion physics. The hydrogen entering the plasma from the wall decreases the mean energy of the ions in the plasma. Besides, the safety of reactors is affected by hydrogen trapping. Tritium can migrate through the walls causing radiation danger. On the other hand, tritium must migrate out of the breeder blanket, otherwise it cannot be used for fueling the reactor. Impurities in the wall materials influence the hydrogen trapping as well.

In this thesis annealing behavior of hydrogen isotopes in carbon based materials was studied. Different models were proposed to describe the experimental profiles. The character of annealing behavior in H and D in implanted samples was found to be the same for both isotopes. Deuterium diffusion in D implanted DLC films can be described by taking into account that atomic D is the diffusing species, whereas D in clusters is immobile. The other model proposed to fit experimental profiles in the Si-free and Si doped DLC takes into account diffusion of free D, thermal detrapping and trapping of D atoms. In Si-DLC films the detrapping process is more simple than in Si-free coatings. However, the activation energy for free D decreases with rising Si concentration in the beginning, but increases in the films with an Si concentration of 33 at.%. Si introduced into the carbon films influences the absorption of deuterium as well. The content of D incorporated in the Si-DLC films during deposition process depends on Si concentration in the films, whereas retention of implanted D in these kind of films is independent on the Si amount.

The graphitization of the carbon films during annealing can be decreased to some extent by the incorporation of Si in the material. Moreover, this leads to the formation of a network which is
stable under thermal treatment and irradiation with heavy energetic ions (coatings with Si content of 33 at.%).

The results demonstrate that doping of carbon based materials with Si can be used to affect the properties of the films and the processes of the trapping, retention and release of the hydrogen isotopes. However, further investigations are needed to find the optimal composition of the material.
ACKNOWLEDGEMENTS

I wish to thank the head of the Department of Physics Prof. Juhani Keinonen, and all the former and current heads of the Accelerator Laboratory, Doc. Armas Fontell, Prof. Jyrki Räisänen, and Doc. Eero Rauhala for providing me the opportunity and challenge to work at the Accelerator Laboratory of the University of Helsinki Department of Physics. I am deeply indebted to my supervisor, Prof. Juhani Keinonen, for his guidance and for placing the facilities of the Department at my disposal.

Many warm thanks are owed to my co-authors, colleagues and the personnel at the Accelerator Laboratory for the pleasant working atmosphere and for their co-operation. My sincere thanks are due to Doc. Kai Nordlund and Dr. Kai Arstila for their advice on using the computer equipment and software. Dr. Pekka Haussalo is gratefully acknowledged for introducing me into ion beam analysis research. I am grateful to Dr. Jari Likonen (Technical Research Centre of Finland) and Dr. Leonid Khriatchev (Department of Chemistry University of Helsinki) for their valuable co-operation during my research.

The experimental part of this thesis work would not be possible without the skillful technical staff of the Laboratory. My special thanks are to Mr. Heikki Sepponen, Mr. Raimo Ingren, Doc. Armas Fontell, Doc. Pertti Tikkanen, Lab.Eng. Kim Wahlström, and Mr. Jari Urkio for the operation of the accelerators, the isotope separator and all the other equipment of the laboratory.

My warmest thanks are due to my parents who brought me up to this world and for their continuous support during all my life. I am also thankful to the friends who have shared with me the moments of joy and sorrow during these years. Last but not the least, I would like to thank my husband Tommy for his patience, understanding and great encouragement every moment during this work. He and our daughter Eva helped me not to forget the world outside the Accelerator Laboratory.

Financial support from the Vilho, Yrjö and Kalle Väisälä foundation is gratefully acknowledged.
Helsinki, April 2000

Elizaveta Vainonen-Ahlgren
References


