

Effect of silicon to deuterium behaviour in DLC

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(July 28, 2000)

This presentation concerns diffusion and retention of deuterium in pure and silicon doped Diamond Like Carbon (DLC) films. The concentration profiles of D were measured by SIMS and elastic recoil detection techniques. Diffusion was studied by annealing the samples in quartz-tube furnace. From these studies it was found out that silicon decreases the amount of retained deuterium in the sample most when Si concentration is 15 at.%. Activation energies for non-trapped D were 1.5 ± 0.2 , 0.7 ± 0.2 , 0.6 ± 0.2 and 1.2 ± 0.2 for samples containing 0, 6, 15 and 33 at.% of silicon respectively.

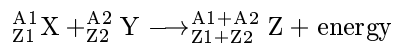
I. INTRODUCTION

Since the advent of fission man has dreamed of using the energy production method of the Sun. After fission became feasible scientists predicted that it'll take only some 20 years to develop a working fusion reactor. That guess proved to be wrong. Today's predictions state that commercial fusion reactor should be in operation at year 2050.

This short article discusses the retention and diffusion of deuterium in Diamond Like Coated (DLC) films. Motivation is to understand how fusion fuel behaves in carbon based composite films which form in the presence of plasma. For complete and thorough discussion of the behaviour of D in DLC films one should check the upcoming article and references therein.¹

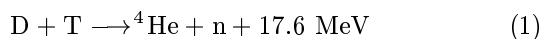
II. BASICS AND UTILISATION OF FUSION

Compared to fission where heavy nuclei are broken apart fusion combines light nuclei to form heavier ones. This process can happen if the sum of binding energies of combining nuclei is lower than the binding energy of resulting nucleus. Fusion is possible for nuclei of mass lower than iron. Basic reaction is easily marked as follows:²



Best example of continuous fusion reaction is that which happens in the Sun. It uses proton-proton fusion to produce ${}^4\text{He}$. Process frees 26.73 MeV/reaction. Looks like small amount, but the energy yield is enormous because there happens $\sim 3.7 \times 10^{38}$ reactions/second in the Sun.³

On the Earth it isn't possible to use p-p reaction because its ignition temperature is too high. Efforts are directed towards deuterium-tritium fusion, which has an ignition temperature of 45×10^6 °C.



The energy released in (1) is lower than in p-p reaction, but enough for us anyway. To control D-T fusion many

different methods have been developed. One of the most important is the Tokamak reactor.

The idea was developed in the 50's by Igor E. Tamm and Andrei D. Saharov. In Tokamak plasma consisted mainly of deuterium and tritium is circling a torus shaped ring. Its contact to walls is inhibited by using strong magnetic fields. Plasma heating can be accomplished with many kinds of methods (microwaves, neutral-injection to name a few). The goal is to reach plasma temperatures and densities high enough to achieve self-sustained reaction. In JET-reactor, England, plasma temperatures of 100 - 200 million °C is reached when density is around $2 - 3 \times 10^{20} \frac{\text{atoms}}{\text{m}^3}$.

Tokamak still has many problems. Some of them are listed below.

PI Sustained reaction: One of the biggest problems is the upkeep of fusion. In functioning reactor the plasma constantly loses energy via radiation and neutron emission. For the time being the energy loss is compensated by feeding more energy to reactor. The goal is a state where energy losses are compensated by the energy of α -particles.

PII Plasma impurities: Magnetic confinement is not impermeable so energetic particles penetrate the field and collide with the walls. Collisions sputter heavier particles which then mix with plasma. Addition of heavy particles (radiated power increases⁴ as Z^3) cools the plasma down and stops reaction. Divertor plates are developed to combat this problem.

PIII Problems with divertors: Divertors are made to direct impurities out from plasma by reshaping the magnetic field so that edge plasma hits the divertors. Therefore the plates meet the greatest amount of incoming plasma particles. Plate material should have low Z and not erode very fast. Other problem is the outdiffusion and retention of D and T which changes D-T ratio of the fuel. This influences reaction effectiveness. Besides tritium retention causes the plates to become radioactive.

III. DIFFUSION IN BRIEF

In this article the term diffusion means movement of atoms or ions in a solid substrate. The phenomenon is totally statistical and governed by temperature. In order to move in a solid an atom needs energy to hop out its current potential well. Higher temperature gives the atom more energy for its disposal and increases the rate of hopping attempts out from the well.⁵

Main equations governing diffusion are Fick's two laws.

$$j(z) = -D \frac{d}{dz} N(z) \quad \text{I}$$

$$\frac{\partial}{\partial z} j(z) = -\frac{\partial}{\partial t} N(z, t) \quad \text{II}$$

ΔE is the activation energy and D is the diffusion constant, which is usually defined

$$D = D_0 e^{-\frac{\Delta E}{kT}}$$

Of course when diffusion is concentration dependent one cannot use this simple diffusion constant. So in this case Fick's laws become more complex. For complete discussion of numerical model used reader is referred to upcoming article.^{1,6}

Basic diffusion mechanisms are substitutional, interstitial and substitutional-interstitial diffusion. The diffusion mechanism exhibited by D in this article is kick-out diffusion which is a derivative of substitutional-interstitial mechanism.⁵

IV. SAMPLES USED

In the study both pure diamond like carbon films (DLC, 40-60% sp³) and DLC films doped with Si were used. Growth process was done in deuterium atmosphere so D incorporated in the samples.⁷ During the first measurements it was found out that increase in Si concentration also increases the amount of retained D in the samples.

Diffusion studies were done by annealing the samples in a quartz-tube furnace at temperatures from 600 to 1050 °C. Annealing time varied between 1 - 24h. Diffusion profiles were measured by SIMS (Secondary Ion Mass Spectroscopy) and TOF-ERDA (Time of Flight - Elastic Recoil Detection Analysis).⁸

V. RESULTS

Deuterium concentration profiles with numerical fits for isochronal annealing (1h) at different temperatures are shown in Fig. 1. From the figure it is easy to see that D starts to diffuse when temperature exceeds 800 °C. The decrease of deuterium concentration in near-surface region is due to thermal desorption. The outdiffusion forms a concentration gradient which starts D diffusion

from the bulk to surface. The decrease of D amount occurs because the diffusion is trap-controlled which means that most of D atoms are bonded or trapped.

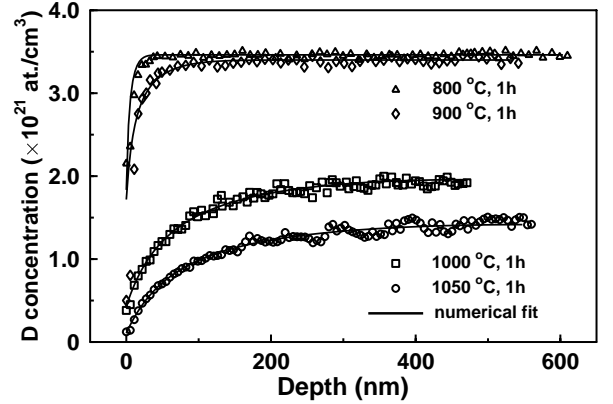


FIG. 1. Deuterium concentration profiles for pure DLC film after isochronal annealing (1h) with numerical fits. The as deposited profile is not presented because it overlaps with the profile of the sample annealed at 800 °C.

Free deuterium migrates fast and because the density of traps is constant untrapped D in the region of high deuterium concentration can travel long distances. Opposite is true for regions of low D concentration where there are large amount of empty traps. The diffusion observed in the Fig.2 looks like it would be concentration or time dependent. Real reason is this trap-controlled method. D only spends more time in mobile configuration at regions of low density of empty traps.

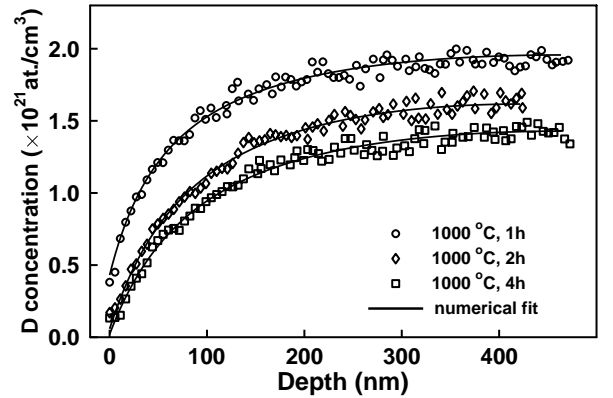


FIG. 2. Concentration profiles of D after annealing Si-free samples at 1000 °C for 1, 2 and 4h

The concentration of retained D in samples with different concentration of Si is presented In Fig.3. Very interesting phenomenon is observed. The deuterium loss from the samples increases when Si is added in DLC. Highest deuterium loss is noticed in samples with Si concentration of 15%. To inspect this let's look at activation energies and the bond structure of the samples.

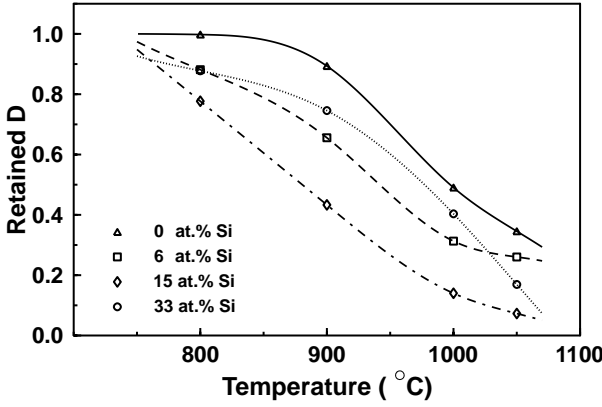


FIG. 3. Amount of retained deuterium as a function of temperature in samples with different Si concentrations. The lines are drawn to guide the eye.

Activation energies of different samples were calculated from Arrhenius plots (Fig. 4). (Activation energy means the minimum energy required for an atom to move from one lattice site to another) These were 1.5 eV for pure DLC, 0.7 and 0.8 eV for samples containing 6 and 15 at.% Si respectively. But the activation energy of sample containing 33 at.% Si was surprisingly higher, 1.2 eV.¹ Conclusion of this effect is that Si decreases the energy barrier for diffusion. One reason is that the density of DLC is almost an order of magnitude higher than the density of Si. Why then 33 at.% Si has higher activation energy? High concentrations of Si changes the bond structure (see below) of material which then causes deuterium to diffuse slower.

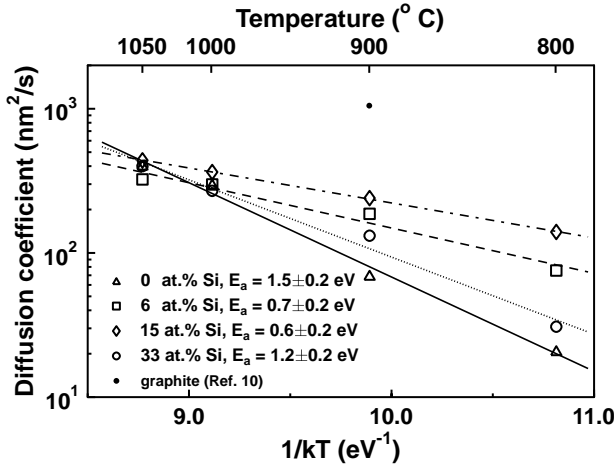


FIG. 4. Arrhenius plot for the diffusion coefficient of non-trapped deuterium. Natural logarithm of diffusion coef. vs. $1/kT$ is shown.

The amount of Si-C bonds was measured by XPS (X-ray photoelectron spectroscopy). As is obvious low Si concentration means also low amount of Si-C bonds (2 and 8% in 6 and 15 at.% Si respectively). Increase of Si concentration to 33 at.% increases the amount of Si-C

bonds to as high percentage as 45%!

The density of traps which was obtained during the fitting process, increases with the increase of Si content. But the density of traps in pure DLC is higher than those of under 15 at.% Si and lower than 33 at.% Si. The density also decreases with increasing temperature. This is maybe because the amount of silicon and carbon dangling bonds decreases due to the new formation of bonds with other Si and C atoms. New bonds are formed because total D concentration decreases.

VI. CONCLUSIONS

Behaviour of deuterium in pure and silicon doped DLC was studied. It was found out that highest D release occurs when Si concentration is 15 at.%. The change of bond structure for samples with Si concentration of 33 at.% supports these findings. Activation energies were obtained from measured diffusion coefficients which exhibit good Arrhenius behaviour

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- ¹ E. Vainonen-Ahlgren, T. Ahlgren, J. Likonen, S. Lehto, T. Sajavaara, W. Rydman, J. Keinonen and C.H. Wu (to be published (2000)).
 - ² J. J. Brehm and W. J. Mullin, *Introduction to Structure of Matter*, 1st ed. (John Wiley & Sons Inc., USA, 1989).
 - ³ W. N. Nottingham and D. A. Greenwood, *An Introduction to Nuclear Physics* (Cambridge University Press, Cambridge, 1986).
 - ⁴ J. Cummings, S. A. Cohen, R. Hulse, D. E. Post, M. H. Redi, and J. Perkins, *Journal of Nuclear Materials* **176**, (1990).
 - ⁵ E. F. Schubert, *Doping in III-IV Semiconductors* (Cambridge University Press, Cambridge, 1993).
 - ⁶ G. D. Smith, *Numerical Solution of Partial Differential Equations: Finite Difference Methods*, 3rd ed. (Oxford University Press, Oxford, 1985).
 - ⁷ E. Vainonen, J. Likonen, T. Ahlgren, P. Haussalo, J. Keinonen, and C. H. Wu, *J. Appl. Phys.* **82**, 3791 (1997).
 - ⁸ E. Vainonen-Ahlgren, T. Sajavaara, W. Rydman, T. Ahlgren, K. Nordlund, and J. Keinonen (to be published in "NATO Advanced Research Workshop" Series, Kluwer, Dordrecht, the Netherlands) (2000).