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Formation of HD molecules during desorption of deuterium from solids

A.A. Pisarev *, Yu.V. Borisyuk, A.V. Varava, V.N. Tsyplakov

Department of Plasma Physics, Moscow State Engineering and Physics Institute, Kashirskoe sh. 31, Moscow 115409, Russian Federation

Abstract

The formation of HD molecules was investigated in experiments on the interaction of deuterium ions and deuterium gas with solids. The influence of vacuum equipment, surrounding surfaces and the target sample itself were analysed and shown to be of importance in different conditions. The HD formation changes the kinetics of deuterium trapping and desorption and must be taken into account when analysing the results of experiments on interaction of deuterium with solids.

1. Introduction

Hydrogen behaviour in solids is of interest for many technological applications including nuclear fusion and is therefore widely investigated in various aspects. Experiments with hydrogen isotopes are often accompanied by isotope mixing and this can be a problem when analysing the dynamics of sorption and desorption processes. Particularly, ion implantation and gas driven experiments on trapping and permeation are often performed with deuterium not to consider effects of residual hydrogen. Nevertheless, it is rather difficult to avoid the influence of protium which can be easily found in various forms in the target sample, surrounding constructions, residual gas, and vacuum equipment. Therefore the mass spectrometer always gives an HD signal. It would not be a problem if the signal did not depend on experimental conditions. But it does depend and this changes the kinetics of sorption–desorption processes and complicates their analyses.

The formation of HD molecules was observed for example in [1–8]. In the present paper we give some of our experimental results on HD formation during heating of solids to show that this process can be important and must be taken into account when analysing hydrogen re-emission, permeation, and thermodesorption.

2. Experimental

We investigated HD appearance in a vacuum chamber when either deuterium ions or deuterium gas interacted with the target sample. Gas discharge ion pumps were used giving the residual pressure of 10^{-6} Pa without annealing of the walls. For ion implantation a mass and energy separated D_2^+ ion beam with the energy of 15 keV (7.5 keV per deuteron) and ion beam density of (1–5) × 10^{14} D^+/cm^2 s were used. The mechanically polished targets were made of Nb, Pd, W, Mo, stainless steel, and graphite. Measurements of HD and D_2 signals in the chamber surrounding the target were performed both during ion implantation and during the subsequent thermal desorption with linear heating. Additionally, samples were heated in a vacuum with a controlled deuterium leakage. In all the experiments the H_2 signal was high. A magnetic mass spectrometer with permanent magnets was used to monitor the partial pressures. The HD and D_2 components were measured in different experimental runs.

3. Results

A striking observation of the HD contribution to desorption was obtained in measurements of thermal desorption spectra from niobium and palladium after D^+ ion implantation. We measured the number of trapped deuterium ions by using the traditional TDS

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* Corresponding author. Tel.: +7-95 323 93 21; fax: +7-95 324 70 24; e-mail: pisarev@plasma.mephi.su.

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(thermal desorption spectroscopy) method monitoring D_2 mass when heating the sample and surprisingly found that there were no D_2 molecules in TDS at low ion fluence. Only at high ion fluence was the desorption of D_2 molecules observed. These facts could lead to a doubt that there was no D^+ trapping at low fluence if it was not so obviously wrong. The explanation came after measurements of HD: it was found that at low ion fluence all the implanted deuterium atoms desorbed back into vacuum during post-implantation heating in the form of HD molecules. Fig. 1 shows the number of deuterium atoms desorbed from Pd in TDS in HD and D_2 molecules as a function of deuterium ion fluence. Desorption as HD dominates at low fluence but becomes a constant at high fluence giving a low contribution to the net desorption rate. Qualitatively the same picture was obtained with Nb. The difference is that D_2 desorption becomes important at a larger fluence than for palladium. For W, Mo, and stainless steel, the HD signal was always small at the level of several percent. There was no difference observed for various brands of Nb and niobium alloys (with Ti and Zr up to several percent).

The second experimental observation is HD formation during ion implantation. When working with graphite and tungsten, it was found that HD signal increases with the implantation temperature as shown in Fig. 2 for graphite. The re-emission rates of HD and D_2 were measured at a high ion fluence characterised by 100% re-emission of the implanted deuterium. At low temperatures HD formation gives only about 5% of the desorption rate, but at above 1000 K it rapidly increases mounting up to 100%. Without measuring the HD fraction, one can make the wrong suggestion about 100% ion trapping at high temperatures.

In measurements of the steady state HD level during D^+ ion implantation in W it was found that the HD signal increases with temperature in different ways in experiments with the virgin and the annealed samples. The virgin, unannealed sample, gave an HD increase at the much lower temperature of about 500 K.

Not only the steady-state levels but also the kinetics of HD and D_2 desorption both during ion implantation and subsequent heating are different as shown in Figs. 3 and 4 for the re-emission from W and TDS from Nb, respectively.

An interesting feature of the re-emission was observed in the beginning of implantation. Measurements on a fresh, unannealed target demonstrated a prompt jump of both HD and D_2 signals just after the ion beam had been switched on. The characteristic time of the jump is very short, and therefore it was discussed in some publications, [9] for example, as a kinetic reflection of ions. Surprisingly, after annealing of the sample, this "reflection" disappeared in D_2 re-emission but survived in the HD re-emission curve, as shown in Fig. 3. The levels of the "reflection" steps in D_2 and HD re-emission curves for the virgin sample were very different: about 5–

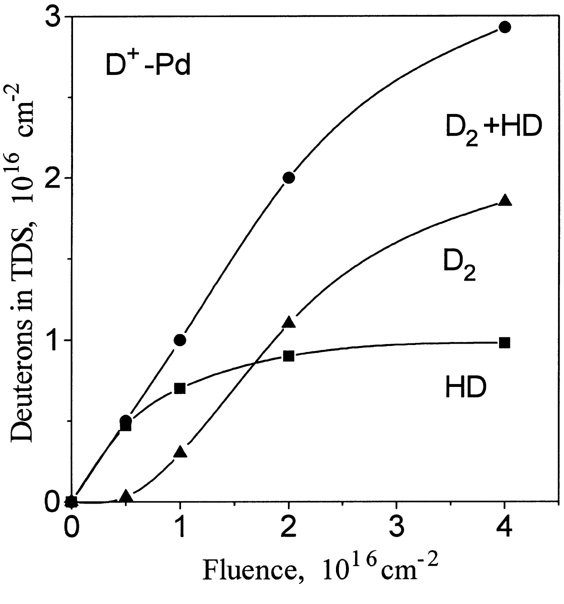

Fig. 1. The number of deuterons desorbed in D_2 and HD molecules measured in TDS after implantation of deuterium ions in Pd. Temperature of implantation 280 K. Energy of ions 7.5 keV/deuteron.

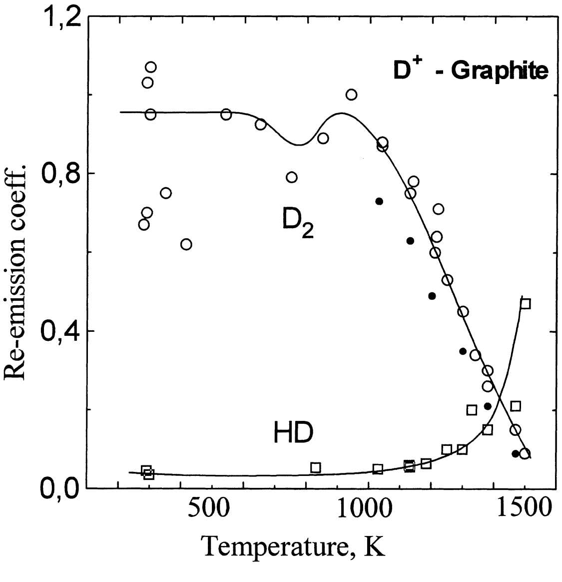

Fig. 2. Steady-state re-emission rate of deuterons which desorb from a graphite during deuterium ion bombardment and detected as D_2 and HD signal rise at different temperatures of bombardment. Circles and squares – for MPG-8; dots – for pyrographite.

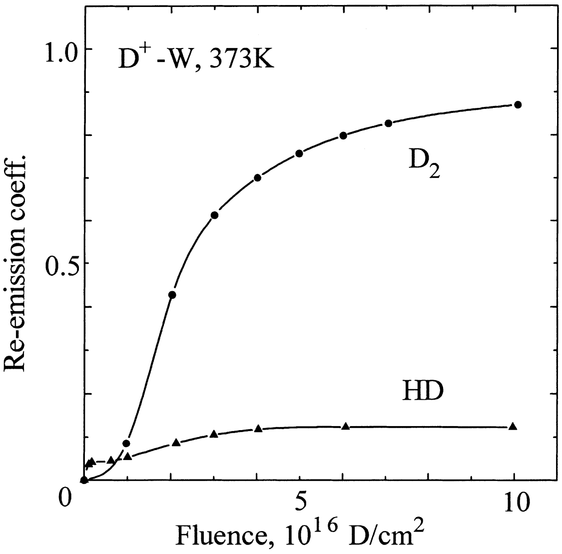

Fig. 3. Re-emission rate of deuterons during deuterium ion implantation in W measured as a rise of D_2 and HD signals as a function of the ion flux. Temperature of implantation is 380 K. Energy of ions is 7.5 keV/deuteron.

10% and up to 50%, respectively. Which of the two values is the reflection coefficient, and is it indeed “reflection”?

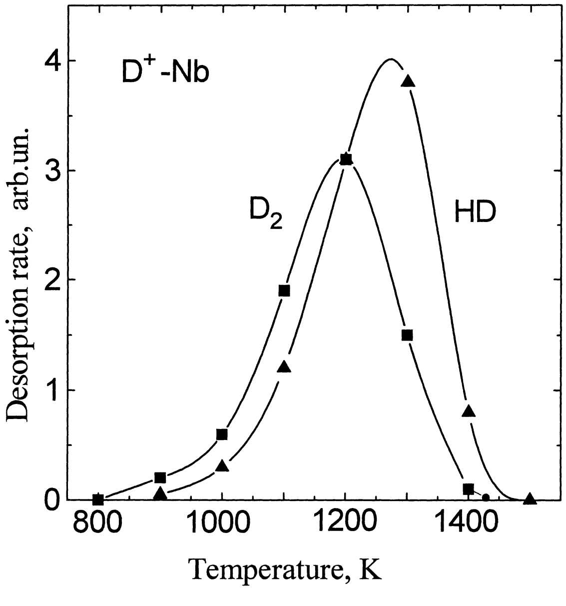

Fig. 4. Thermal desorption spectra of deuterium after deuterium ion implantation in Nb. Measurements are performed for HD and D_2 masses. Temperature of implantation is 280 K. Energy of ions is 7.5 keV/deuteron. Ion fluence is 3×10^{17} deuteron/cm^2 s.

Additional experiments were performed without ion bombardment. Pre-annealed samples were just heated in vacuum after exposure in the gas of low pressure (about 10^{-5} Pa). It was found that during exposure in the gas, metals absorbed residual deuterium and protium giving rise to thermal desorption during subsequent linear heating of the sample. Fig. 5 shows a TDS of D_2 after exposure of Nb in deuterium gas at two temperatures. The position of the D_2 TDS peak corresponds to that in Fig. 4. If to take a fresh unannealed sample and measure HD TDS after exposure in D_2 repeatedly several times, one can find that after several cycles of heating, there were no HD desorption from stainless steel, possibly due to the loss of pre-abosorbed protium. Niobium and especially graphite steadily gave HD from run to run. An increase of both H_2 and D_2 pressures in vacuum around the target leads to an increase of the HD signal.

4. Discussion

Formation of HD molecules can take place in the vacuum equipment used, on the surrounding walls, and on the surface of the target sample and in its bulk.

As for the first term, it includes the mass spectrometer, vacuum gauge, and vacuum ion pumps where electron impact and thermal dissociation of H_2 and D_2 molecules along with ionization lead to HD formation on the surrounding surfaces. Indeed, an increase in the ionization efficiency in the spectrometer, gauge, and pumps was found to increase the HD signal. Nevertheless, the contribution of the apparatus effect is not the

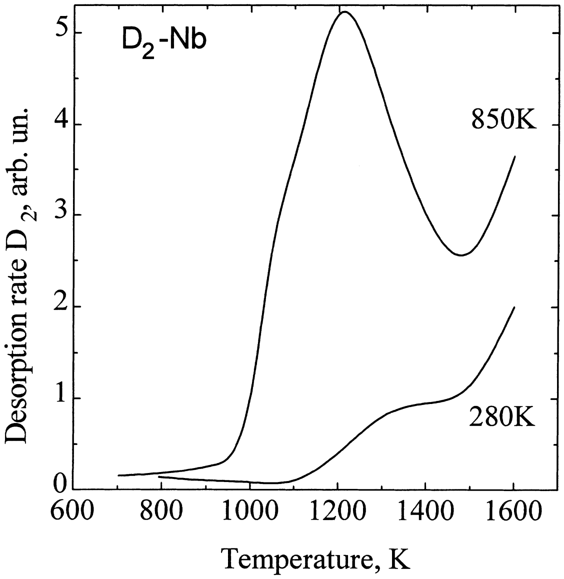

Fig. 5. Thermodesorption of D_2 from Nb after 1 h exposure in D_2 at 5×10^{-5} Pa at temperatures of 280 and 850 K.

only one. At least, in saturation during ion implantation, the HD signal is as high as several tens of percent. To reach this value due to ionization in the equipment, it is necessary to provide the respective level of dissociation and ionization in vacuum. This seems to be an unrealistic condition. Sometimes in TDS we do not observe D_2 at all and one cannot expect that 100% of D_2 molecules are dissociated or ionized in gas and that the probability of the reverse D–D recombination is zero on the surfaces of the vacuum equipment. Otherwise, we would see neither the D_2 signal in the residual gas nor its change in the experiment. Besides, the HD/D_2 ratio depends on the temperature of the sample, the ion fluence, and the pre-history of the sample. Finally, we changed the vacuum pumps: we substituted a diffusion pump for an ion pump and found that HD signal in TDS after exposure in deuterium was about the same and sometimes becomes even higher due to worse vacuum. Thus, it is not the vacuum equipment that is only responsible for the HD signal.

The second possible HD source is isotope mixing on the walls. If desorption from the sample is supposed to be of the molecular form, one can hardly expect a high rate of mixing on the cold surrounding walls. Besides, all the dependencies on the target conditions are not in favour of this source. The "reflection" jump of HD can be explained by influence of the surrounding surfaces. The deuterons reflected from the target bombard the surrounding walls. Some of them become trapped, some reflect again and again until they come to rest. The energetic particles can stimulate desorption of D_2, H_2 and HD from the surrounding walls which are functions of H and D concentrations on the walls. Unfortunately in this picture one cannot explain why the "reflection" of D_2 depends on the pre-history of the target.

The next possibility is H–D mixing on the surface of the sample (or in its bulk if the molecular state in the bulk is possible). If so, one can easily explain many observations. For example, the fluence dependencies of the number of HD and D_2 molecules in TDS from Nb, Pd, and W are obvious: the higher the heat of solution (negative for Nb, positive for W and intermediate for Pd), the lesser the concentration of absorbed protium, the lesser the H/D ratio, and the lesser the HD content in spectra. TDS from Nb does not contain D_2 until a higher ion fluence than TDS from Pd, while those from W always contains a D_2 signal which is higher than that of HD. Measurements of the re-emission rate from W in the initial stage of implantation, Fig. 3, give a higher value of HD compared with D_2 because the concentration of the implanted deuterium is small. In these experiments either absorbed or adsorbed protium participates in mixing with the implanted deuterium. If the sample was pre-annealed to desorb protium dissolved in the virgin material, its re-appearance in the sample seems to be connected with sorption from the residual vacuum between the cycles of implantation and annealing. Protium from the surrounding gas can also actively participate in mixing at high temperatures during implantation in the saturation regime. The rapid increase in HD at high temperatures can be ascribed to the increase in the dissociation probability of gas molecules on the surface. We observed an exponential increase of the HD formation rate with the increase of the target temperature during annealing of W in H_2 and D_2 mixture, and this can be due to thermal activation of the dissociative chemisorption followed by H–D mixing and desorption.

An alternative explanation of the HD signal during ion implantation can be given if taking into account the experimental observation described in [10]. By using the time-of-flight mass-spectrometry, it was found that atoms but not molecules desorb from the target. Hence, the HD molecule can be formed at the walls surrounding the target due to recombination of the reflected deuterium atom with an adsorbed protium atom. It is important that the general tendencies in the temperature dependencies of D emission in [10] and the HD signal in Fig. 2 are similar. Hence, one can accept this explanation for ion implantation at high temperatures.

At the same time one must mention that HD was observed also in the TDS spectra from W even at low temperatures. One can hardly explain HD formation in this experiment by atomic emission: there is neither thermal activation at low temperature nor ion stimulation after termination of bombardment. Therefore, one may suppose that HD molecules are formed at the target surface due to recombination of the implanted deuterium atoms with adsorbed protium atoms coming onto the surface either from the bulk of the target or from vacuum. One must mention the obvious tendency by comparing Nb, Pd, and W: the number of HD molecules in the thermal desorption spectra from these materials decreases in this sequence.

5. Conclusion

The formation of HD molecules was observed in experiments on the interaction of D^+ ions and D_2 gas with various materials, e.g. Nb, Pd, W, Mo, SS, and graphite. The HD signal was observed during D^+ ion bombardment, during exposure in D_2 gas, and during heating after interaction with ions or gas. Three sources seem to contribute to HD yield in different situations: vacuum pumps and the mass spectrometer, the surfaces surrounding the target sample, and the target itself. The quantity of deuterium desorbed as HD can be as high as about 100%. The dynamics of HD evolution differ from that of D_2. Therefore the effect of isotope mixing must be taken into account when analysing experimental data on the behaviour of hydrogen isotopes in materials.

Acknowledgements

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