Experimental determination of the deuterium binding energy with vacancies in tungsten

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M. Zibrov [a, b, c, *], S. Ryabtsev [a], Yu. Gasparyan [a], A. Pisarev [a]

[a] National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe shosse 31, 115409 Moscow, Russia
[b] Max-Planck-Institut für Plasmaphysik, Boltzmannstraße 2, D-85748 Garching, Germany
[c] Gent University, Sint-Pietersnieuwstraat 41, B-9000 Gent, Belgium

HIGHLIGHTS

- Deuterium interaction with vacancies in tungsten was studied experimentally.
- A set of TDS measurements was performed at different heating rates.
- The binding energy of deuterium with vacancies in tungsten was determined directly.

ARTICLE INFO

ABSTRACT

Deuterium (D) interaction with vacancies in tungsten (W) was studied using thermal desorption spectroscopy (TDS). In order to obtain a TDS spectrum with a prominent peak corresponding to D release from vacancies, a special procedure comprising damaging of a recrystallized W sample by low fluences of 10 keV/D ions, its annealing, and subsequent low-energy ion implantation, was utilized. This experimental sequence was performed several times in series; the only difference was the TDS heating rate that varied in the range of 0.15—4 K/s. The sum of the D binding energy (E_b) with vacancies and the activation energy for D diffusion (E_D) in W was then directly determined from the slope of the Arrhenius-like plot $\ln(\beta/T_m^2)$ versus $1/T_m$, where β — heating rate and T_m — position of the respective peak in the TDS spectrum. The determined value of $E_b + E_D$ was 1.56 ± 0.06 eV.

1. Introduction

Tungsten (W) will be used as a plasma-facing material in the divertor region in ITER, and its use in future fusion devices is currently likely. Due to a very low solubility of hydrogen (H) isotopes in W, the presence of various lattice defects (vacancies, vacancy clusters, voids, dislocations, grain boundaries, impurities) strongly influences H isotope retention in W [1]. Therefore parameters of trapping, particularly hydrogen trapping/detrapping energies and detrapping attempt frequencies, are essential for predicting H isotope transport and retention in W plasma-facing

components. So far, however, there is no general agreement about these values. For instance, the value of the detrapping energy for the first trapped H atom in a single vacancy in W varies among researchers in the wide range of 1.29—1.79 eV [2—11].

Calculations of the hydrogen-defect interaction are often performed by using the density functional theory (DFT) [5—11]. Experimental investigations of the hydrogen-defect interaction are often performed by thermal desorption spectroscopy (TDS), and the parameters of the interaction are obtained by fitting numerical calculations based on diffusion-trapping codes to experimental thermal desorption spectra [3,4,12—17]. Aside from the uncertainties of the thermal desorption measurements [18,19], a large uncertainty in the determination of characteristics of trapping sites in this approach is given by the fact that a result of a TDS spectrum simulation depends on many input parameters in the numerical model (H detrapping energy, H diffusivity in the material, trap concentration profile, initial distribution of trapped H,

recombination rate at the surface). As a result, one experimental spectrum can be fitted by using many combinations of fitting parameters [4]. However, under the condition of a high H−H recombination rate at the surface, the H binding energy with a defect can be directly determined from the shift of the desorption maximum in a series of TDS measurements performed with identical samples but with different heating rates [20,21].

The most common problem of TDS experiments is the interpretation of the types of defects responsible for particular peaks. Therefore it is essential to investigate samples having only one dominant and well-known defect type. In the case of irradiation of metals by light ions with energies in the keV range, mainly point defects (Frenkel pairs − single vacancies and interstitial atoms) are formed as the energy transfer from an incident ion to a metal atom is relatively low; thus, dense collision cascades are not formed [22]. At low irradiation fluences (corresponding to low damage levels), the concentration of created vacancies is small; therefore, at the temperatures when their mobility is low, the fraction of vacancy clusters is small [3,23,24].

In the present contribution, this approach is used for direct determination of the deuterium (D) binding energy with single vacancies in W from TDS measurements with different heating rates.

2. Theory

The energy state of a H atom near a trapping site is schematically shown in Fig. 1. Here, by the binding energy E_b we denote the difference in the potential energy of a H atom in a trap and in a solution site. By the activation energy for trapping E_{tr} we mean the energy barrier for a H atom to enter a trap. By the detrapping energy E_{dt} we mean the energy barrier for H escape from a trap, which is defined as $E_{dt} = E_b + E_{tr}$. In the particular case when the activation energy for trapping E_{tr} is equal to the activation energy for H diffusion E_D, the sum $E_b + E_D$ is equal to the detrapping energy E_{dt}. The activation energy for trapping in Fig. 1 is shown to be less than the activation energy for diffusion $E_{tr} < E_D$, but the opposite case of $E_{tr} \geq E_D$ is also possible.

As the surface effects can retard hydrogen release and thus complicate TDS analyses, we will assume and consider only the case of a very fast H−H recombination at the surface, so that the surface
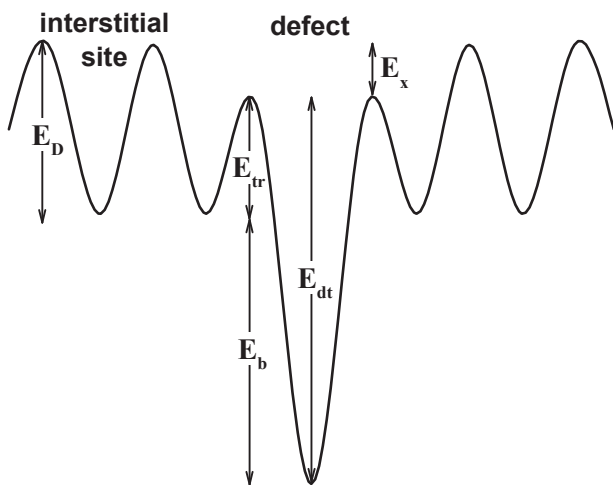
effects do not influence both the TDS peak position and its shape. In this case two limiting H release regimes were identified: detrapping-limited regime and retrapping-limited regime [20]. In the former case, the concentration of traps N_t (in atomic fractions) is so low ($N_t \ll (\lambda/\Delta)^2$, where λ - lattice constant, Δ - characteristic location depth of trapped H) that a H atom after release from a trap diffuses to the surface without being retrapped by other traps. In the latter case, the concentration of traps is high enough ($N_t \gg (\lambda/\Delta)^2$), so a H atom released from a trap can be retrapped many times by empty traps before reaching the surface.

In the case of the detrapping-limited regime the relation between the H detrapping energy E_{dt} from a defect, the heating rate β during TDS, and the respective peak position T_m in a TDS spectrum, is expressed in the following way [20]:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\nu_{dt}\frac{k}{E_{dt}}\right) - \frac{E_{dt}}{k}\frac{1}{T_m},\tag{1}$$

where ν_{dt} − the detrapping attempt frequency, k − Boltzmann constant.

In the case of the retrapping-limited regime, the equation is the same, but the sum $E_b + E_D$ appears instead of E_{dt}:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\nu_{eff}\frac{k}{E_b + E_D}\right) - \frac{E_b + E_D}{k}\frac{1}{T_m},\tag{2}$$

where ν_{eff} − the effective detrapping attempt frequency, which depends both on the properties of the trapping sites and of the bulk.

Thus, depending on the release regime, either the detrapping energy E_{dt} or the sum $E_b + E_D$ can be directly determined from the slope of the Arrhenius-like plot $\ln(\beta/T_m^2)$ versus $1/T_m$ in a series of TDS measurements performed using identical samples and different heating rates (the so-called Kissinger method [25]). One should note that in this approach no prior knowledge of the trap profile, the initial distribution of trapped hydrogen, and the material properties is required − the only requirement is a sufficiently high recombination rate at the surface [21]. In addition, this method allows to determine either E_{dt} or $E_b + E_D$ independently of the detrapping attempt frequency ν_{dt}, while this is not possible in fitting of numerically simulated TDS spectra to experimental ones where the value of ν_{dt} has to be assumed (typically assumed to be of the same order of magnitude as the lattice vibration frequency, i.e. $\sim 10^{13}$ s^{-1}).

Although all the considerations described above were made for a metal containing only one type of trapping sites (characterised by the values of E_b and E_{tr}) and each trap can accommodate only one H atom, the same dependences are valid for every trap type in the metal as long as they do not evolve during the TDS measurements. The same dependencies should be also valid in the case of trapping of several H atoms by each trap since it can be approximated by several distinct trapping sites [20]. From the experimental point of view, in the case of a material with several types of trapping sites, TDS peaks must be well-resolved to determine their positions accurately.

3. Experimental details

3.1. Experimental setup

The experiments were carried out in the MEDION ion-beam facility (MEPhI, Moscow) [26]. An ion beam is extracted from a duoplasmatron ion source, passes through an einzel lens, is mass-separated in a 60° deflection magnet, and then directed onto a

Fig. 1. Potential energy diagram for a H atom near a defect in a metal, where E_{dt} − the detrapping energy, E_b − the binding energy, E_{tr} − the activation energy for trapping, E_D − the activation energy for diffusion, and E_x − the difference between the activation energy for trapping and the activation energy for diffusion.